Adsorption of methylene blue (MB) from aqueous solution using mixed sorbents prepared from Date pit and Olive stone

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ABSTRACT

The present study focuses on the recovery of the mixed waste food « the date pits and olive stones» in the field of industrial liquid effluent treatment.

The materials was mixed and used in their native form to improve their adsorptive capacity. A rang of physicochemical analysis was performed, for the characterization of adsorbents used, among them: FTIR spectroscopy. In order to test the performances of these adsorbents we are interested in cationic dye the methylene blue considered as pollutant. The effects of several parameters such as contact times, initial concentration of dye, solution pH, and temperature and the proportion of date pits and olive stones in the mixture, were studied in batch system. The result showed that the contact time for removal of all the dyes is about ten minutes, for different concentration of the solution studied colour. For a pH range that varies between 3 and 10, it was found that a large percentage removal of dye was found for pH values above 4. Modelling of experimental results was performed using models of Langmuir and Freundlich isotherms, which show that adsorption follows the Langmuir model with high correlation coefficients.

1. INTRODUCTION

Today, with technological development, and progress that have various vital sectors. The various industrial activities are constantly increasing, and produce liquid effluents, which are often contaminated with toxic and harmful substances.

Among the industries that generate significant pollution, the textile industry which discharges are mostly loaded dyes (H. Zollinger., 1987,G. Mishra et al., 1993) which gives sensation to pollution serious enough. This industry represents only two-thirds of the total production of dyes, about 10 to 15% of dyes used, are discharged through the effluent (H. Zollinger., 1987).

The latter, loaded with dye, can have harmful effects, and severe impacts in the receiving environment, as they can affect the activity of photosynthesis in aquatic life, due to the reduction of light penetration. And can also be toxic to some aquatic species, due to the presence of aromatic hydrocarbon, metals, and chloride in their constitutions, which are toxic (G. Mishra et al., 1993, I.M. Banat et al., 1996).Thus the removal of dyes from these effluents has become a major environmental concern today (H. Zollinger., 1987).

Current methods used for disposal, include physicochemical methods such as flocculation, oxidation, ozonation, and reverse osmosis, and biological techniques (T. Robinson et al., 2001). All these methods are different in terms of color removal, operation and financial costs (Khan.A Tabrez et al., 2004.,8 W FC et al., 2001). In recent years researchers are directed to methods of treatment using natural materials such as clays, soft commodities, due to their low cost (Robinson, T et al., 2001).

The date pites and olive stones are products of agricultural waste, available in our country rejected large amounts annually to the environment.

In the present work, we opted for recovery of the mixture of by-products of agriculture date pits and olive stones, and their use as adsorbents for the treatment of effluents containing dye, for it was used as a dye methylene blue to test adsorptive capacity of adsorbents.

2. MATERIALS AND METHODS

Sorbent preparation

The date pits were collected from the south of Algeria, and the olive stones were obtained from an olive oil production in the north region of Algeria. These materials used in our study, were first washed several times with tap water to remove dust and dirt adhering, then rinsed with distilled water. They were then exhausted with hexane to remove residual oils and then repeatedly washed with distilled water and dried at 105°C, then they were crushed.

Once crushed different sample based on a mixture of the two materials were prepared. For this the two materials were mixed in the following way, we fixed the mass of date pits and vary the mass of olive stone, which will allow us to obtain the samples given in table 1.

Table. 1 : Different proportion of date pits and olive stones in the mixture

Sample number	Mass of date pits (g) (DPN)	Mass of olive stone (g) (OSN)
1	5	1
2	5	2
3	5	3
4	5	4
5	5	5
6	0	5
7	5	0

DPN: date stone in the native state ; OSN : olive stone in the native state

The mixture simple of date pits and olive stones were milled with an electric grinder, then sift through a stack of sieves of different mesh openings. The study focused on size fraction between (80 μ and 630 μ). Then we kept them in desiccators until use.

We worked with the simples in their native state.

Adsorbate : The dye used in this study is a cationic dye is methylene blue (MB), it is chosen because of their strong adsorption on solids.

The chemical structure of methylene blue is shown in Fig1

Fig1 Structure of Methylene Blue

The colored solutions are prepared by dissolving dye in distilled water at a concentration of 1000mg/ l. The experimental solutions were obtained by diluting the concentration for the desired concentrations.

Structural analysis by FTIR spectroscopy: in the range of $[400 \text{ and } 4000 \text{ cm}^{-1}]$, were taken in order to find out which functional groups are responsible for the biosorption process. IR spectroscopy analyses were performed using a Fourier transform spectrometer type "" Nicolet 560 FTIR coupled to a digital computer for the route spectra between $[400 \text{ and } 4000 \text{ cm}^{-1}]$.

Batch adsorption experiments

Adsorption equilibrium and kinetic experiments were determined by contacting a known amount of the mixture of date pits and olive stones (0.1g), with 30ml of methylene blue solution (MB) in sealed glass bottles. At 20°C , pH 5.6 and stirring speed of 300rpm/mn.

The tests were stopped when equilibrium is reached. The samples are filtered through a filter paper and the concentration is measured by a UV-visible spectrophotometer. The fixed amount of dye per gram of adsorbent is given by the following relation:

$$q_t = (C_i - C_f) V/m$$

Where q is the uptake (mg/g), C_i is the initial methylene blue concentration, C_f is the final MB concentration (mg/g), V is the solution volume (ml), m is the mass (g) of the mixture (date pits and olive stones).

The effect of initial dye concentration ranging from 50 to 600mg/l was studied.

The effect of solution pH was studied by performing the adsorption experiments of MB at different pH levels (3,4,5,6,7,8,9 and 10). The solution pH adjustment was achieved by addition of appropriate amounts of either 0.1N HCl or 0.1 N NaOH solutions.

Experiments were conducted at 20, 30,40 and 50°C in order to investigate the effect of temperature on the adsorption process. The adsorbent concentration was always kept constant at 100mg/l and adsorption was followed till reaching equilibrium.

3. RESULTS AND DISCUSSION

IR spectra analysis

IR analysis of mixture was used to identify some characteristic functional groups of the mixture adsorbent of date pits and olive stones for the adsorption process. The profiles of IR spectroscopy for the mixture of date pits and olives stones was showed in fig.2

Fig 2 : IR spectroscopy for mixed sorbent (mixture of date pits and olive stones)
(DPN: date stone in the native state, OSN : olive stone in the native state)

Adsorption isotherm

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose (B.H. Hameed et al, 2007).

Several models have been published in the literature to describe the experimental data of adsorption isotherms. The Langmuir and Freundlich are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentration.

Freundlich isotherm

The Freundlich isotherm describes the non-ideal adsorption of a heterogeneous system and reversible adsorption (Freundlich, 1906). The model can be expressed as

$$q_e = K_F C_e^{1/n} \quad (1)$$

Eq. (1) can be linearized by taking logarithms:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (2)$$

Where q_e is the amount of dye adsorbed per unit of adsorbent ($\text{mg} \cdot \text{g}^{-1}$), C_e is the concentration of dye solution at adsorption equilibrium ($\text{mg} \cdot \text{L}^{-1}$), and K_F ($\text{L} \cdot \text{g}^{-1}$) and n is the Freundlich adsorption isotherm constants. The result of adsorption isotherms modelling by Freundlich model were represented in fig 3, The favourable adsorption in this model can be characterized by the fact that if a value for n is above unity, adsorption is favourable and a physical process (N.Babakhouya et al, 2010).

Table 2 indicated that the value of n varies between 4 and 6 at different proportion of the mixture of date pits and olive stones, this indicated favourable sorption of dye onto the different mixture of waste materials.

Fig3 : Freundlich plot for adsorption of MB on différent mixed sorbent

Langmuir isotherm

Langmuir's isotherm model suggests that uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm equation is represented by the following equation (M.Gouamid et al, 2013)

$$C_e/q_e = 1/bQ + C_e/Q \quad (3)$$

where q_e is the amount adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of the adsorbate ions (mg/L), Q and b are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and energy of adsorption, respectively. When C_e/q_e is plotted against C_e , a straight line with slope $1/Q$ and intercepts $1/bQ$ is obtained (Fig.4).

Fig 4 : Langmuir isotherm plot for the adsorption of MB on different mixture adsorbent

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L , defined as [Deepak pathania et al,2013]):

$$R_L = 1 / (1 + bC_0) \quad (4)$$

where C_0 is the highest initial solute concentration, b is the Langmuir's adsorption constant (L/mg). The R_L value implies the adsorption to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Value of R_L were varied in the rang of 0.045 and 0.078 with several proportion of mixed adsorbent. The value of R_L is between 0 and 1 showed that the adsorption of MB was favourable with the different mixture of date pits and olive stones used. Maximum theoretical uptake upon complete saturation of the surface of the mixture (5g DPN+1g OSN) of date pit and olive stone was obtained to be 75,188 compared to 70,4225 for olive stone only.

Table 2 : Langumuir and Frendlich isotherm constants for methylene blue onto different proportion of mixture of date pits and olive stones

Mixed adsorbent	Langmuir parameter				Freundlich parameter		
	qm (mg/g)	b x10 ²	R2	RLx 10 ²	KF	1/n	R2
5g DPN+1g OSN	64,5161	5,08	0,9922	4,6916	21,6023	0,1805	0,9845
5g DPN+2g OSN	72,9927	3,77	0,9805	6,2206	20,7539	0,203	0,972
5g DPN+3g OSN	67,1141	3	0,9811	7,6885	19,0283	0,1962	0,9018
5g DPN+4g OSN	75,188	2,95	0,9859	7,8197	17,7828	0,23	0,948
5g DPN+5g OSN	70,922	5,24	0,9955	4,5572	21,513	0,2008	0,9742
OSN	70,4225	1,98	0,9637	11,2112	13,9701	0,2499	0,7664
DPN	84,7458	3,09	0,9969	7,84	24,6547	0,2199	0,9409

OSN : olive stone in native state. DPN : date pit in native state

Adsorption kinetics

The figure shows the evolution of the adsorbed amount with time. The adsorption of the dye (MB) on different mixture of adsorbents used has the same gaits characterized by a strong adsorption on the first few minutes of contact. According to the figures, in the first 10 minutes, the percentage removal of methylene blue was fast. After it stabilizes and reaches equilibrium. The first rapid phase may be due to the availability of vacant adsorption site at initial stage. The high percentage of elimination of dye was observed in the mixture (5g DPN+ 5g GON) with 29.029mg/g compared to the mixture (5g DPN+ 3g OSN) with 27.536mg/g. and the uptake for olive stone only was 24,7237mg/g,

Fig 2 : The effect of contact time to the adsorption rate of MB by the mixture of adsorbents

in order to investigate the mechanism of adsorption, the kinetic data were treated with the pseudo-second order kinetic model. The differential equation is the following:

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (5)$$

where k_2 is the equilibrium rate constant of pseudosecond- order adsorption (g/mg min). Integrating Eq. (5) for the boundary condition $t = 0$ to t and $q_t = 0$ to q_t , gives the following:

$$1/(q_e - q_t) = 1/q_e + k_2 t \quad (6)$$

which is the integrated rate law for a pseudo-second-order reaction. Eq. (6) can be rearranged to obtain a linear form:

$$t/q = 1/(k_2 q_e^2) + (1/q_e) t \quad (7)$$

The slope and intercept of the plot of t/q versus t were used to calculate the second-order rate constant, k_2 (Fig. 3). It is more likely to predict the behavior over the whole range of adsorption for the case of chemisorption mechanism as the rate controlling step

Fig 3 : Pseudo second order kinetics of MB by the mixed sorbent ($C = 100\text{mg/l}$, $T = 20^\circ\text{C}$)

Table 3 lists the results of the rate constant studies for different initial dye concentrations by the second-order models. The correlation coefficient, R^2 for the pseudo-second-order adsorption model has high value ($>99\%$), and its calculated equilibrium adsorption capacity, $q_{e,cal}$ is consistent with experimental data. These facts suggest that the pseudo-second-order adsorption mechanism is predominant, and that the overall rate of the dye adsorption process appears to be controlled by the chemisorption process.

Table 3 : Pseudo-second order kinetics model parameters for MB sorption onto the mixture of date pits and olive stones

proportion of the mixture	Equation pseudo seconde ordre			
	qe,exp (mg/g)	qe,cal (mg/g)	k2 (g/mg.min)	R2
5g DPN+1g OSN	28,5033	28,5714	0,0406	0,999
5g DPN+2g OSN	28,2455	28,169	0,0708	0,9991
5g DPN+3g OSN	27,5369	27,7778	0,0932	0,9986
5g DPN+4g OSN	28,6965	28,169	0,0435	0,9971
5g DPN+5g OSN	29,0831	28,9017	0,016	0,9984
OSN	24,7237	25,2525	0,0342	0,9986
DSN	29,3837	29,4985	0,0333	0,9998

The effect of pH of the solution

the effect of the dye solution plays an important role in the whole adsorption process, particularly on adsorption capacity. The effect of pH is studied for an initial concentration of 100mg / l. The pH range is selected between [3-10]. (Fig 5) shows that the adsorption capacity is minimum at pH = 3, and increases with increasing pH up to pH = 4 and then remains almost constant between pH values between 4 and 10. At acidic pH, the adsorption capacity is low, this is due to the presence of excess H⁺ ions, which are competing with dye cations BM⁺ for adsorption sites, which causes the decrease adsorption capacity.

At high pH, greater than 4, the surface of the adsorbent can become negatively charged, there by improving the electrostatic attractive forces between the surface of the adsorbent and the BM⁺ cations. Then the acid pH is unfavorable for the adsorption of methylene blue. (Fawzi Banat et al, 2003.,Oualid Hamdaoui,2006).

Fig 5 : Effect of initial pH in the dye sorption capacity by the mixed sorbent (C = 100mg/l, T=20°C)

Adsorption thermodynamic

The thermodynamic parameters for the adsorption process, the standard free energy, standard enthalpy and standard entropy were calculated using the following equations (Zhang Jian et al, 2013)

$$\Delta G = -RT \ln K_L \quad (5)$$

$$\Delta G = \Delta H - T \Delta S \quad (6)$$

$$\ln K_L = \Delta S/R - \Delta H/RT \quad (7)$$

where ΔG is the standard free energy, kJ mol^{-1} ; R is the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; T is the absolute solution temperature, K ; ΔH is the standard enthalpy, kJ mol^{-1} ; ΔS is the standard entropy. The standard enthalpy and standard entropy values can be calculated from the slope and intercept of the plot of $\ln K_L$ versus $1/T$ as shown in Fig. 6. The values of these parameters were calculated using Eqs. (5), (6) and (7). at various temperature and were shown in Table 4.

Table 4 showed that the value of H was positive indicating the endothermic nature of the adsorption of methylene blue onto the mixture (5g DPN+1g OSN) different temperature. And the value of H was negative for all the rest of mixture sorbent indicate an exothermic process, similar result has been reported by (Vipasiri vimonses et al, 2009). The positive value of S inferred the affinity of the mixture (5g DPN+1g OSN) adsorbent for methylene blue as a result of the increased randomness at the interface between the solid-liquid phases, but for the rest of mixture adsorbent, the negative value of S suggest a decrease in randomness at their solid/solution interface and no significant changes occur in the internal structure of the adsorbents through the adsorption. (Vipasiri vimonses et al, 2009., Necip Atar et al, 2007)

In general, the range of standard free energy for physisorption is in a range of -20 to 0 kJ/mol , and the chemisorption varies between -80 and -400 kJ/mol (Vipasiri vimonses et al, 2009)

The values of G were all negative at difference temperature, for all mixture adsorbent indicating that the adsorption was spontaneous and physical.

Fig6 : Relation between equilibrium constant (K_c) and temperature ($C_0= 100\text{mg/l}$)

Table 4: Value of the thermodynamic of adsorption at various temperatures and for different proportion of mixture ($C_0 = 100\text{mg/l}$)

mixed sorbent	T° (°C)	$\Delta G^\circ(\text{Kj/mol})$	$\Delta H^\circ(\text{KJ/mol})$	$\Delta S^\circ(\text{Kj/molK})$
5g DPN+1g OSN	293	-8,078	93,059	0,342
	303	-6,821		
	313	-18,205		
	323	-15,633		
5g DPN+2g OSN	293	-7,459	-52,831	-0,15
	303	-9,644		
	313	-6,49		
	323	-3,283		
5g DPN+3g OSN	293	-5,546	-39,304	-0,109
	303	-9,041		
	313	-6,02		
	323	-2,626		
5g DPN+4g OSN	293	-7,548	-90,381	-0,275
	303	-10,512		
	313	-5,625		
	323	0,366		
5g DPN+5g OSN	293	-6,839	-8,643	-0,007
	303	-5,587		
	313	-8,296		
	323	-5,66		
OSN	293	-7,345	-21,103	-0,048
	303	-6,072		
	313	-5,247		
	323	-6,098		
DPN	293	-6,472	-19,55	-0,044
	303	-7,096		
	313	-3,794		
	323	-6,163		

4. CONCLUSION

The aim of this work was the preparation of an adsorbent by mixing the two adsorbents date pits and olive stones to improve their adsorptive capacity. The mixed sorbent were investigated for the removal of basic dye namely methylene blue from aqueous solution.

The adsorption equilibrium of methylene blue onto the mixture of date pits and olive stone was represented by Langmuir and Freundlich isotherm, the adsorption isotherm data were well fitted by the Langmuir model. And the thermodynamic study shows that the sorption onto the mixture of date pit and olive stone was spontaneous and exothermic.

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